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MEMORANDUM FOR IN-HOUSE PUBLICATIONS

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SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-**TP**-1998-**093**
J. Mills and J. Boatz Theoretical Determination of the Heats of Formation of Selected High-Energy Molecules" **HEDM Conference Presentation** **(Statement A)**

Theoretical Determination of the Heats of Formation of Selected High-Energy Molecules

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Introduction–

As a measure of the intrinsic energy content of a substance, the standard enthalpy of formation constitutes a critical parameter in the evaluation of the likely performance of candidate rocket fuels and propellant additives. The gas-phase heats of formation, $\Delta H_f^\dagger$, of a series of unusual strained and substituted organic molecules have been determined in a progression of semi-empirical, *ab initio* and density functional calculations and the results have also been compared with common non-computational estimates.

Methods–

- Depth of Treatment (increasing expense and presumed accuracy)

  I. No computation

  II. Semi-empirical Computation

  III. Hartree-Fock or DFT Geometry Optimization

  IV. Hartree-Fock or DFT Minimum Energy and Hessian

  V. MP2 Energy (at HF Geometry) and HF Hessian

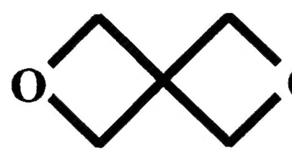
  Exp. Experiment

- **Type of Approach–Determination of $\Delta H_f^{\dagger}$ from:**

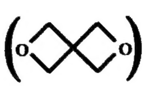
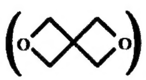
  A. Investigation of the Target Molecule Alone

  B. An Isodesmic (Bond-Preserving) Reaction or a Higher Analogue:

  e.g.

  $4\,CH_4 +$  $\rightarrow 2\,CH_3\text{–}O\text{–}CH_3 + C(CH_3)_4$

  Gas-phase enthalpy of formation at 298 K:

$\Delta H_f^{\dagger}$() $\equiv \Delta H_{f,\,gas,\,298K}$()

$$= \Delta\left(\Delta H_f'^{\dagger}\right) - \left[\Delta E_{eq} + \Delta E_{zp} + \Delta\left[H_{298K} - H_{0K}\right]\right]$$

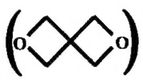
With:

$$\Delta\left(\Delta H_f^{\prime\dagger}\right) = \sum_{\substack{i', \text{ molecules} \\ \text{except target}}} \nu_{i'}\, \Delta H_f^{\dagger}(i')$$

$$= 2\,\Delta H_f^{\dagger}(\mathrm{CH3\text{-}O\text{-}CH_3}) + \Delta H_f^{\dagger}(\mathrm{C(CH_3)_4}) - 4\,\Delta H_f^{\dagger}(\mathrm{CH_4})$$

$$\Delta E_{eq} = \sum_{\substack{i \\ \text{molecules}}} \nu_i\, E_{eq}(i)$$

$$= 2\,E_{eq}(\mathrm{CH_{\cancel{3}}\text{-}O\text{-}CH_3}) + E_{eq}(\mathrm{C(CH_3)_4}) - 4\,E_{eq}(\mathrm{CH_4})$$

$- E_{eq}($  $)$

$$\Delta E_{zp} = \sum_{\substack{i \\ \text{molecules}}} \nu_i\, E_{zp}(i)$$

$$\Delta\left[H_{298K} - H_{0K}\right] = \sum_{\substack{i \\ \text{molecules}}} \nu_i \left[H_{298K}(i) - H_{0K}(i)\right]$$

- **Individual Methods**

Method IA

Benson–Group (and Atom) Additivity Rules (Empirical Parameterization)

$$\Delta H_f^{\dagger} = \sum_{\substack{j \\ \text{groups}}} \Delta H_{f,j}$$

S.W. Benson, *Thermochemical Kinetics*, Second Ed., (Wiley, New York, 1976), and works cited therein.

Method IIA

$\Delta H_f^{\dagger}$ Directly from Semi-Empirical Code

Method IIB

Semi-Empirical Energies and Thermodynamics

$\Delta H_f^{\dagger}(i')$–exp.; $E_{eq}(i)$–semi-empir. calc.; $\Delta E_{zp}(i)$–scaled SE;

$\Delta[H_{298K}(i)-H_{0K}(i)]$–exp. (if avail.) or scaled SE

Method IIIA

Ibrahim and Schleyer–Method of Hartree-Fock Atom Equivalents (Empirical/Theoretical Correlation)

$$\Delta H_f^{\dagger} = E_{HF} + \sum_{\substack{j \\ \text{atoms}}} \Delta E_j$$

M.R. Ibrahim and P.v.R. Schleyer, *J. Comp. Chem.*, 6, 157 (1985); some parameters added by present author.

Method IIIB

Hartree-Fock or DFT Energies with SE Thermodynamics

$\Delta H_f^{\dagger}(i')$–exp.; $E_{eq}(i)$–HF/DFT; $\Delta E_{zp}(i)$–scaled SE;

$\Delta[H_{298K}(i)-H_{0K}(i)]$–exp. (if avail.) or scaled SE

Method IVB

Hartree-Fock or DFT Energies and Thermodynamics

$\Delta H_f^\dagger(i')$–exp.; $E_{eq}(i)$–HF/DFT; $\Delta E_{zp}(i)$–scaled HF/DFT;

$\Delta[H_{298K}(i)-H_{0K}(i)]$–exp. (if avail.) or scaled HF

Method VB

MP2 Energies and HF Thermodynamics

$\Delta H_f^\dagger(i')$–exp.; $E_{eq}(i)$–MP2; $\Delta E_{zp}(i)$–scaled HF;

$\Delta[H_{298K}(i)-H_{0K}(i)]$–exp. (if avail.) or scaled HF

Method Exp

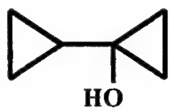
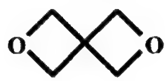
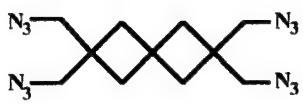
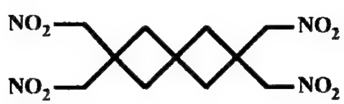
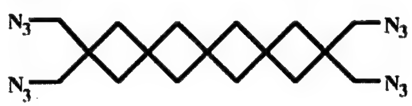
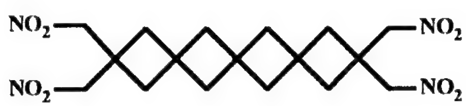
Experiment (or, if not available, high level theory, (*e.g.*, G2 or variant)

Semi-empirical and *ab initio* calculations performed using serial and parallel GAMESS on IBM RS/6000 work stations at Air Force Re-
search
serach Laboratory, and tens of nodes of the IBM SP computers at the Maui High Performance Computing Center and U.S. Army Engineer Waterways Experiment Station. Gaussian 94E on the Silicon Graphics/Cray Origin 2000 at the Aeronautical Systems Center, Major Shared Resource Center, was employed for the density functional calculations. The longest program step consumed around 40 node days.

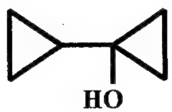
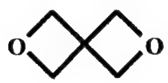
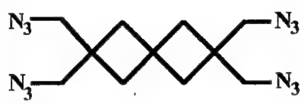
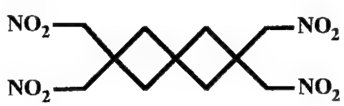
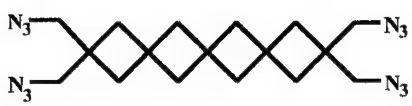
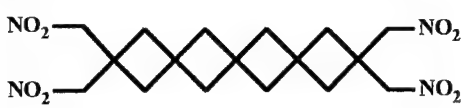
(Semi-empirical calculations employed the PM3 Hamiltonian, *ab initio* calculations within the 6-31G(d) basis, and DFT, the B3LYP functional. Scale factors for vibrational energies: HF-0.89, PM3-0.97, DFT-0.96.)

Results–

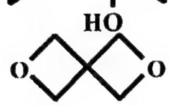
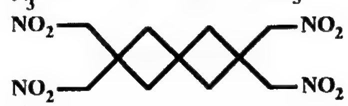
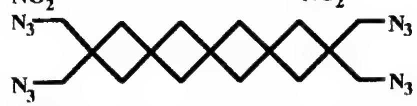
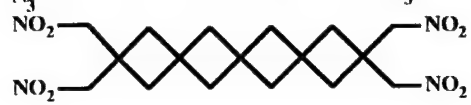
$\Delta H_f^{\dagger}$ (kcal/mol) of Target Molecules (Series A)

Molecule	IA	IIA	IIIA
	86.6	74.0	83.8
	-8.5	-5.4	-9.1
	-26.9	-44.6	-30.2
	320.6	306.8	281.1
	-19.8	-26.1	-27.4
	354.3	316.2	308.7
	13.9	-18.1	-1.4
RMS vs. VB	11.9	13.2	19.0

Hartree-Fock $\Delta H_f^{\dagger}$(kcal/mol) of Targets (Series B)

Molecule	IIB	IIIB	IVB	VB
	82.1	82.5	75.1	76.5
	-12.2	-9.9	-9.9	-10.2
	-25.4	-27.4	-29.8	-28.8
	332.5	333.9	329.3	315.8
	-12.5	-15.7	-18.8	-34.7
	348.0	365.0	358.0	342.7
	1.5	13.7	8.4	-8.6
RMS vs. VB	11.6	15.7	11.7	

DFT $\Delta H_f^{\dagger}$ (kcal/mol) of Targets (Series B)

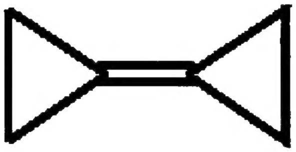
Molecule	IIIB	IVB
	80.1	72.8
	-11.9	-11.7
	-29.9	-32.4
	329.5	323.6
	-24.5	-28.5
	357.2	347.8
	2.1	-4.0

Conclusions–

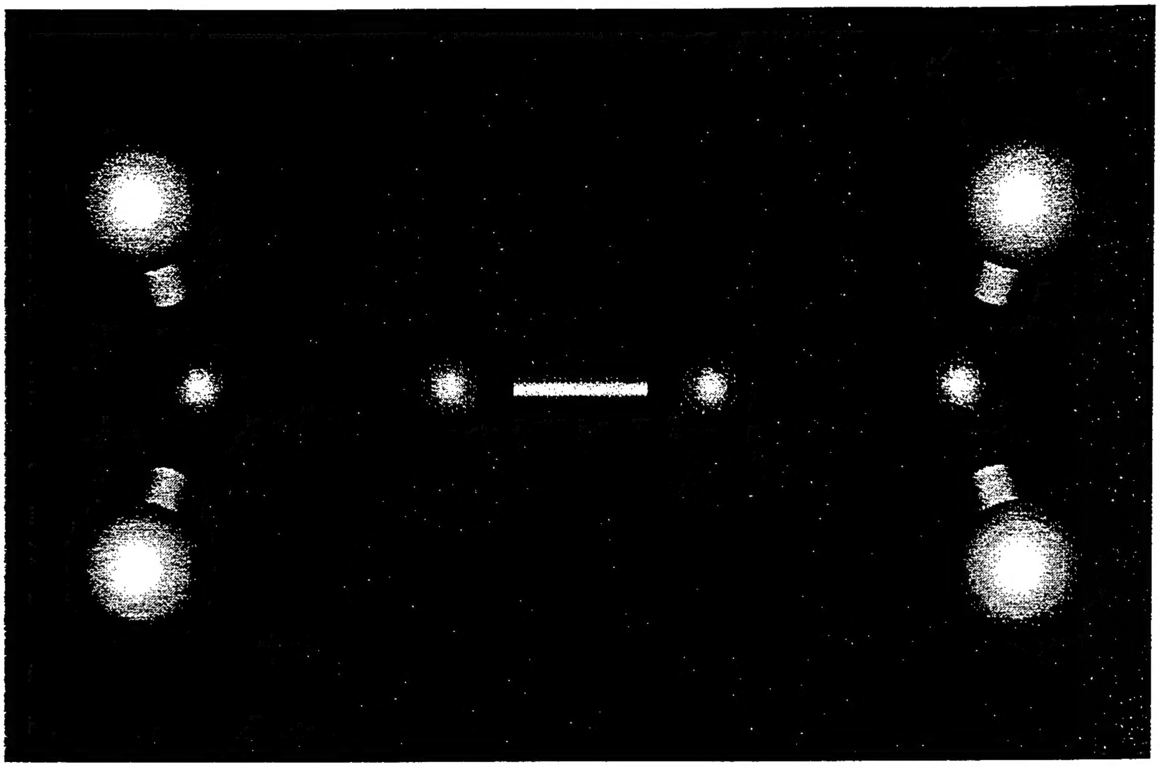
The accuracies of a series of progressively more expensive and sophisticated theoretical methods for calculating gas-phase enthalpies of formation have been evaluated in a specialized reference set. This procedure provides parameters which, when combined with information about condensation energetics, are fundamental to quantitatively model the performance of actual propellant formulations. However, in addition, this also justifies means of economically and efficiently screening large sets of, perhaps rather speculative, compounds at a relatively low level, so as to allow valuable experimental and theoretical resources to be focused upon candidates of particular promise.

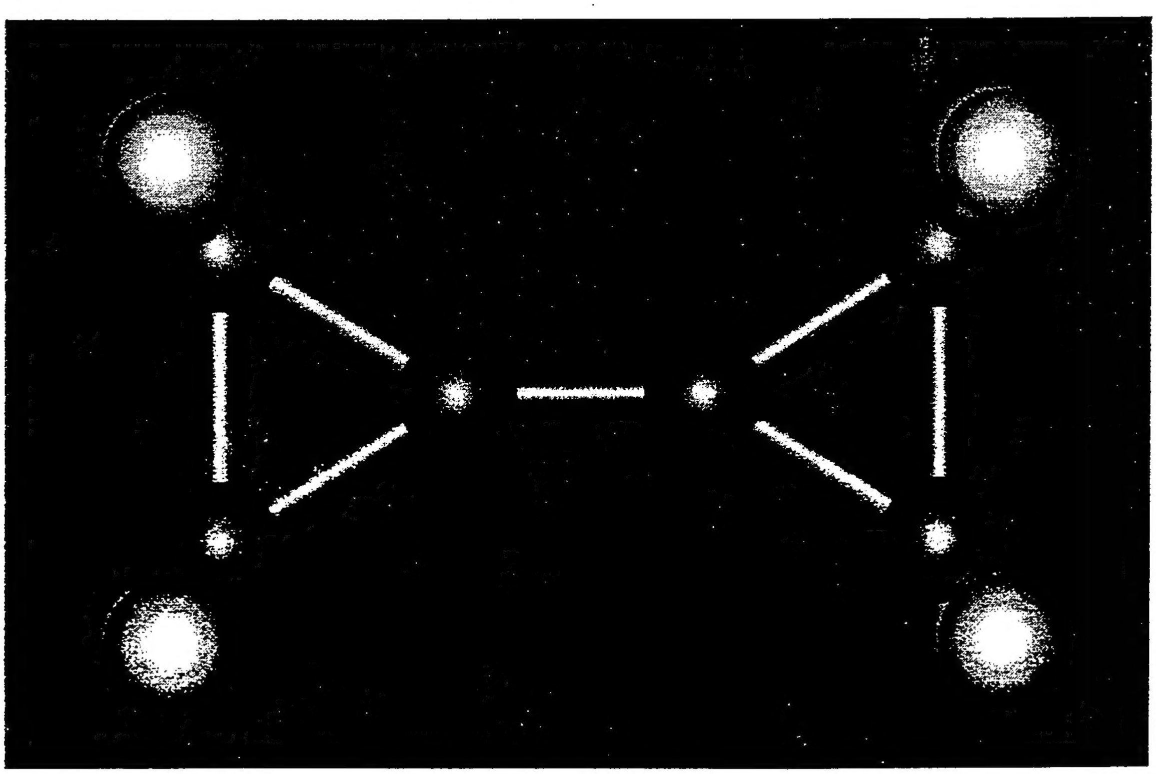
Acknowledgments–

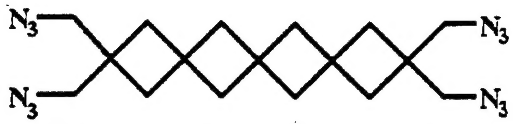
The Maui High Performance Computing Center and the U.S. Army Engineer Waterways Experiment Station provided computational resources on their IBM/SP computers through the DoD High Performance Computing Challenge Project Initiative. The Aeronautical System Center, Major Shared Resource Center provided time on their Silicon Graphics/Cray Origin 2000.



C_6H_8 (106 basis functions) D_{2h}







$C_{17}H_{24}N_{12}$ (483 bf.) S_4